

# CHARACTERIZATION OF LEAD AND CADMIUM SPECIES IN EMISSIONS FROM MUNITIONS DEACTIVATION FURNACE

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## ABSTRACT

Information on the chemical species, and phase and particle size distribution of lead and cadmium species is required for developing strategies for pollution prevention, environmental compliance, and mitigation strategies for controlling hazardous air pollutant emissions from Army munitions deactivation furnaces. Emissions samples were collected from the furnace exhaust system on a small arms deactivation furnace at Tooele Army Depot, Tooele, Utah. The samples collected were analyzed using standard U.S. Environmental Protection Agency methods and other laboratory chemical and physical methods to obtain particulate size distribution and to identify lead and cadmium species. Results show that lead is a major component of the particulate matter while antimony is a distant second. Lead oxides and carbonates are the dominant species. Cadmium is not a major component in the emissions for the two munitions deactivated. The results showed that nearly 45-58% of the particulate emissions are of particulate matter PM<sub>2.5</sub>.

## 1. INTRODUCTION

The Army releases hazardous air pollutants into the atmosphere from its weapons demilitarization and training activities. Of significant concern is the fine particulate material (PM<sub>2.5</sub>) containing lead and cadmium that is generated by demilitarization furnaces. The Army currently uses ceramic baghouses to control these emissions from its demilitarization furnaces. The maintenance of these baghouses can be expensive when the candle filters become plugged. ERDC-CERL is developing new control technologies to lessen the maintenance requirements and to reduce the overall metal emissions to surroundings. Knowledge of the various metal species present in the emissions may help with development of effective emission control technologies designs, efficient means of operation of the furnace, and pollution prevention strategies. Thus,

ERDC-CERL has conducted a sampling study on the conventional demilitarization furnace APE 1236 at the Tooele Army Depot.

## 2. EXPERIMENTAL APPROACH

A schematic of the deactivation furnace is shown in Figure 1. The samples were collected at near isokinetic conditions in a temperature range of 400 to 1600 °F. Samples were collected at three different locations [(1) after the cyclone, (2) on the duct before the ceramic filter house, and (3) on the stack after the ceramic filter house] on the furnace exhaust system. Due to the regulatory importance of the semi-volatile metals, an emphasis was placed on characterizing the lead and cadmium species, which are expected to be in the form of aerosols or particulates after combustion. Emissions sampling was conducted while two types of munitions were deactivated to determine composition, phase distribution, and particle size distributions.

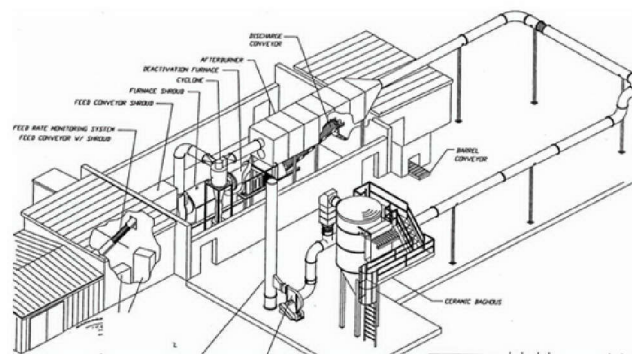


Fig. 1: Schematic of a conventional small arms deactivation furnace.

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### 3. ANALYTICAL METHODS

Analytical procedures/methods were established for identification and quantification of the major chemical species (lead and cadmium oxides, sulfides, sulfates, nitrates, nitrites, chlorides, and metals of lead and cadmium), and particle size and distribution of the particles. Gaseous fractions and particulate fractions were collected in solutions and quartz filters. These fractions were subjected to further solubilization and extractions to identify anions and cations apart from identification of metals. Filterable particulate matter samples were collected on quartz fiber filters for analyses using X-ray fluorescence (XRF), X-ray diffraction (XRD), atomic absorption spectroscopy, ion chromatography (IC), inductively coupled argon-plasma spectroscopy (ICP) and for elemental and organic carbon (EC/OC) analyses.

### 4. RESULTS

The results show that lead is by far the predominant component of the particulate matter. Antimony is a distant second, with lead oxides and carbonates being the dominant species. An estimated 40% of the total filter mass was quantitatively identified. The XRD analyses indicated that a large fraction of the weight gain (> 25%) was of a crystalline form that could not be identified. An additional large fraction (>30% of the weight) was non-crystalline and was suspected to be lead-bearing. There was a major contribution by lead mono-oxide (litharge) and a minor contribution of lead carbonate hydroxide. Other expected contributing lead oxides include  $Pb_2O_3$ ,  $Pb_3O_4$ ,  $PbO_2$ , and  $Pb_2O$ . The oxygen in these compounds can account only for up to 4% of the unidentified filter mass. These observations may be interpreted to infer that < 45% of the total filter weight gain was in the form of lead oxide. Lead nitrates ( $Pb(NO_3)_2$  and  $Pb(OH)NO_3$ ) and nitrites ( $3PbO \cdot N_2O_5 \cdot H_2O$ ) could account at most for an additional 15% of the total unidentified mass collected on the filters. A few components that are expected to significantly contribute to the remaining 60% of the mass captured on the filters were not analyzed. Oxygen, nitrogen, silica, and water (hydrating other molecules) are the primary components of concern.

Off-gases from the natural gas combustion, combined with excess air fed to the burners and in-leakage to the exhaust system, will generally include fairly large amounts of the following gases: oxygen (15 to 16% in the stack gas), carbon dioxide (3.5 to 4.5% in the stack gas), nitrogen (approximately 80% in the stack gas), nitrogen oxide, nitrogen dioxide, water (approximately 5% in the stack gas), and carbon monoxide (approximately 1 to 2 ppm in the stack gas).

Carbon is prevalent in the combustion gas as well as in the propellant. However, the organic carbon and elemental carbon analyses of the filter catches indicated that an average of less than 1% of the filter mass was composed of carbon, almost all of which was organic carbon. An average of less than 0.04% of the filter weight gain was identified as inorganic carbon. Hydrocerussite ( $Pb_3(CO_3)_2(OH)_2$ ) was positively identified as a minor component of the filter catch by the XRD analyses.

Sulfur was not found on the filters in significant quantities by XRF. Sulfate was measured by ion chromatography in the water-soluble fraction of the filter catch as the third highest component on the filter.  $PbS$ ,  $PbSO_4$ ,  $PbSO_4 \cdot PbO$ ,  $Pb(HSO_4)_2 \cdot H_2O$ ,  $PbS_2O_8 \cdot 3H_2O$ , and  $PbSO_3$  are the possible sulphur-lead compounds.

Figure 2 is a typical particle size analysis data collected from a filter immediately after the after burner. Nearly 45% of the mass on the filter is in the form of PM<sub>2.5</sub>. The fraction of PM<sub>2.5</sub> increases to 58% for the sample collected after the baghouse.

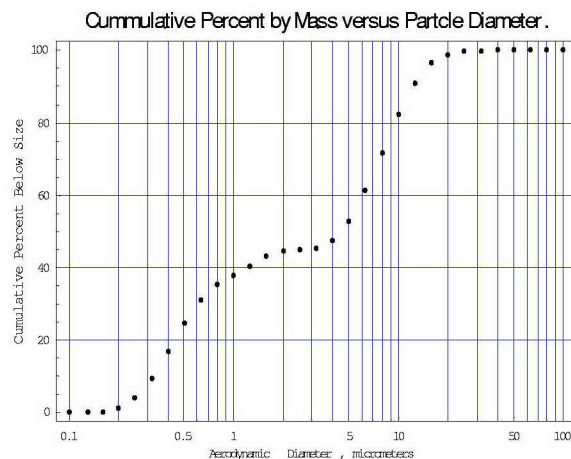


Fig. 2. Cumulative Percent by Mass vs. Particle Diameter (sample collected after the afterburner, for 20-millimeter ammunition)

### CONCLUSION

The lead and cadmium emissions from the combustion processes are generally believed to be predominantly in the form of aerosols or particulates. The results show that lead is by far the predominant component of the particulate matter. Antimony is a distant second, with lead oxides and carbonates being the dominant species. This information can be used to design intervening processes to enhance particle growth or agglomeration or introduce other chemical species to form environmentally benign species to reduce overall impact of the hazardous air pollutants released from munitions deactivation furnaces.